



LETTER

Direct effects of CO₂ and temperature on silicate weathering: Possible implications for climate control

PATRICK V. BRADY¹ and SUSAN A. CARROLL²

¹Geochemistry Research, Sandia National Laboratories, Albuquerque, NM 87185, USA

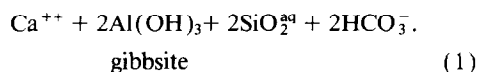
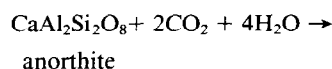
²Earth Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

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Abstract—A critical uncertainty in models of the global carbon cycle and climate is the combined effect of organic activity, temperature, and atmospheric CO₂ on silicate weathering. Here we present new dissolution rates of anorthite and augite which indicate that silicate weathering in organic-rich solutions is not directly affected by soil CO₂ but is very sensitive to temperature. Apparently CO₂ accelerates silicate weathering indirectly by fertilizing organic activity and the production of corrosive organic acids. The weathering dependencies highlight the ability of silicate weathering to act as a global thermostat and damp out climate change, when used as input in steady-state carbon cycle and climate models.

INTRODUCTION

OVER GEOLOGIC TIME ($T > 10^5$ y) accelerated weathering of silicate minerals in response to global warming is seen as a critical feedback control on global climate because weathering of the crust consumes CO₂, causing atmospheric CO₂ levels and greenhouse effect temperatures to decrease (WALKER et al., 1981; LOVELOCK and WHITFIELD, 1982; BERNER et al., 1983; VOLK, 1987; RAYMO et al., 1988; MARSHALL et al., 1988; CALDEIRA and KASTING, 1992; VELBEL, 1993). A general silicate weathering reaction is



Silicate dissolution in soils is driven by biologically produced carbonic and organic acids (e.g., BASU, 1981; STUMM et al., 1983; GRANDSTAFF, 1986; KNOLL and JAMES, 1987; BENNETT, 1991; WOGELIUS and WALTHER, 1992; WELCH and ULLMAN, 1993). Dissolved CO₂ is one of the most abundant acids in soils where root respiration and organic degradation raise carbon dioxide levels to 10 to 100 times that of the atmosphere (e.g., HOLLAND, 1978).

Calculated climatic conditions depend on the rate at which CO₂ is consumed by the weathering of the continents. Global carbon cycle models used to calculate P_{CO_2} in the geologic past (and distant future) differ most of all in the weathering rate- P_{CO_2} feedback mechanisms they use as inputs (VOLK, 1987; MARSHALL et al., 1988; BERNER, 1991; SCHWARTZMAN and VOLK, 1989; VELBEL, 1993). All with the exception of BERNER et al. (1983) rely to some extent on silicate weathering rates measured in the laboratory. Partly as a result of the difference in the weathering functions, predicted climate sensitivities do not agree. All models have weathering rates

increasing with temperature, though the numerical relation between the two is seldom the same. With the exception of the BLAG model (BERNER et al., 1983), most have rates at a given temperature being proportional to $P_{\text{CO}_2}^{0.3}$. This relation, originally derived from high temperature (100–200°C) feldspar dissolution experiments (LAGACHE, 1965), has since been used to model the effects that carbonic acid (VOLK, 1987), pH (SCHWARTZMAN and VOLK, 1989), and biologic activity (MARSHALL et al., 1988) have on the quantity of CO₂ consumed by the weathering of Ca and Mg silicates. This is probably unfounded, because at low temperatures the direct effects of CO₂ on weathering, soil pH, and biologic activity are unknown.

RATE DEPENDENCIES

A first step to understanding the biogeochemical factors controlling the global carbon cycle and climate is to understand the weathering feedback mechanism. We have determined the temperature and P_{CO_2} sensitivities of augite and anorthite weathering in organic acid solutions characteristic of soils. Augite and anorthite are useful analogues for crustal Mg and Ca silicates, respectively. Acetic acid is a common organic acid in soils which is known to accelerate silicate dissolution (GRANDSTAFF, 1986; SVERDRUP, 1990).

Weathering rates of augite measured in 10^{-3} M acetic acid solutions at 25, 35, and 60°C, saturated at atmospheric and 100% CO₂ are shown in Fig. 1. Anorthite rates were measured at 21, 35, and 60°C. In the augite runs pH was maintained at pH 4 (± 0.05) by adding HCl. Output pH values for the anorthite runs at atmospheric P_{CO_2} was 4.02 (21°C), 3.97 (35°C), and 3.92 (60°C). Uncertainty in the pH measurements was ± 0.04 or less. Output pH values for the 100% CO₂ runs were only slightly (0.03 pH units) less than those done at atmospheric P_{CO_2} and within the uncertainty of the pH measurements.

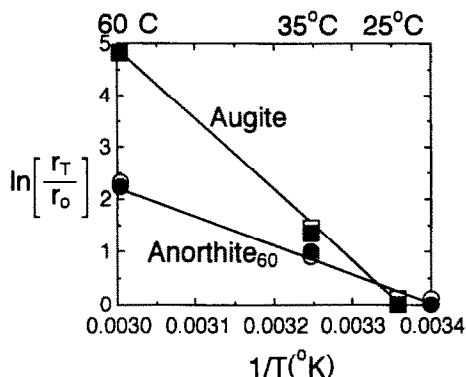


FIG. 1. Temperature dependent dissolution rates, r_T (moles Si/cm²) of augite (squares) and anorthite (circles) as a function of reciprocal temperature (Kelvin) and P_{CO_2} relative to their reference values, r_0 , at 25°C (augite) and 21°C (anorthite). The closed and open symbols represent $P_{\text{CO}_2} = 10^{-3.5}$ and 1 atm, respectively. 2 g of HF-H₂SO₄ etched (SCHOTT et al., 1981) augite (Na_{0.07}Mg_{0.37}Ca_{0.95}Fe_{0.58}Mn_{0.04}Al_{0.05}Si_{1.98}O₆) from Hybla, Ontario, Canada were reacted in 10⁻³ M acetic acid solution with a continuously stirred, thermostatted Mettler DL12 autotitrator, started to pH 4. Augite rates were calculated from the linear release of Si as a function of time. 1 g of anorthite (An₆₀), washed in distilled, deionized H₂O to remove fines was reacted in thermostatted single pass flow-through reactors (KNAUSS and WOLERY, 1986) where the dissolution rate is proportional to the net increase in [Si] multiplied by the solution pumping rate.

Rates are strongly dependent on temperature yet the effect of CO₂ is minimal. The lack of a direct CO₂ effect on weathering is a new and critically important result. It is generally accepted that weathering depends on the amount of carbon dioxide in solutions weathering silicates (e.g., HOLLAND, 1978). Figure 1 indicates that CO₂ does not directly control silicate weathering. Any acceleration of silicate weathering by soil carbon dioxide must therefore arise through CO₂ fertilization of organic activity. Increased organic activity should result in increased production of corrosive organic acids and a higher overall rate of silicate weathering (VOLK, 1987; SCHWARTZMAN and VOLK, 1989; BERNER, 1991).

An indirect effect of increasing atmospheric CO₂ on weathering is to raise global temperatures through the greenhouse effect (e.g., MANABÉ and STOUFFER, 1980). The lines in Fig. 1 are least squares fits to the rates using the integrated Arrhenius equation,

$$\frac{r_T}{r_0} = \exp \left[\frac{E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right], \quad (2)$$

where r_T and r_0 are the dissolution rate at temperature T (in Kelvin) and at reference temperature T_0 , respectively. E_a is the dissolution activation energy (kcal/mol), and R is the gas constant. Activation energies for augite and anorthite dissolution in acetic acid solutions are 27.5 and 11.5 kcal/mol, respectively. Therefore, we write the range of temperature-dependence for Ca and Mg silicate weathering as

$$\exp \left[\frac{11500}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \leq \frac{r_T}{r_0} \leq \exp \left[\frac{27500}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]. \quad (3)$$

Ca Silicates Mg Silicates

Note that temperature-dependent anorthite and augite rates measured in acetic acid solutions are roughly comparable to Ca and Mg silicate rates measured in organic-free solutions; dissolution activation energies for the latter are on the order of 10 to 20 kcal/mol (BRADY, 1991). Our measured temperature dependencies also bracket the temperature dependency of silicate weathering measured in the field from streamwater chemistry data; $E_a = 18.4$ kcal/mol (VELBEL, 1993). It is therefore reasonable as a first approximation to use the laboratory temperature dependencies as input in global carbon cycle models.

IMPLICATIONS FOR CLIMATE MODELS

Global temperature variations are relatively small (less than 10°C); hence, Eqn. 3 can be approximated by

$$\exp \left[\frac{\Delta T}{15.34} \right] \leq \frac{r_T}{r_0} \leq \exp \left[\frac{\Delta T}{6.41} \right]. \quad (4)$$

Ca Silicates Mg Silicates

In Fig. 2 we have compared our experimentally calibrated weathering expression with that of MARSHALL et al. (1988) and with the updated feedback of BERNER (1993, 1994; $E_a = 15$ kcal/mol). Each of the latter models considered the constraints that weathering puts on climate over the past 100 million years. Mg silicate weathering is much more temperature dependent than Ca silicate weathering indicating that the weathering feedback is dependent on crustal composition and may be stronger than previously thought. This has important implications for models of the global carbon cycle. To show this we use it as input in existing models which calculate atmospheric CO₂ in the geologic past (BERNER, 1991). Figure 3 compares paleo- P_{CO_2} values calculated with

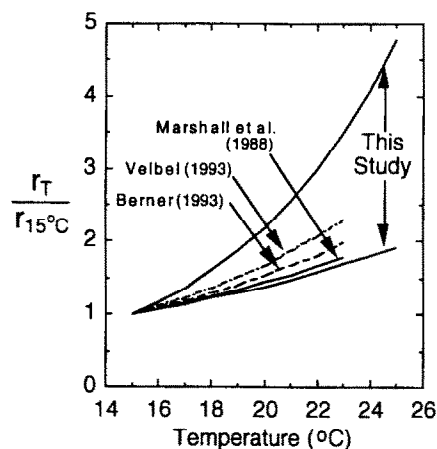


FIG. 2. Weathering rates as a function of temperature. $r_T/r_{15^\circ\text{C}}$ is the ratio of weathering rates referenced to their values at 15°C. The weathering function of this study (4) is plotted along with those of MARSHALL et al. (1988); $r/r_0 = \exp(\Delta T/13.7)$ and BERNER (1993, 1994), $E_a = 15$ kcal/mol. The thick lines indicate the weathering function determined in this study. Also shown is the weathering function of VELBEL (1993), corresponding to an activation energy of 18.4 kcal/mol.

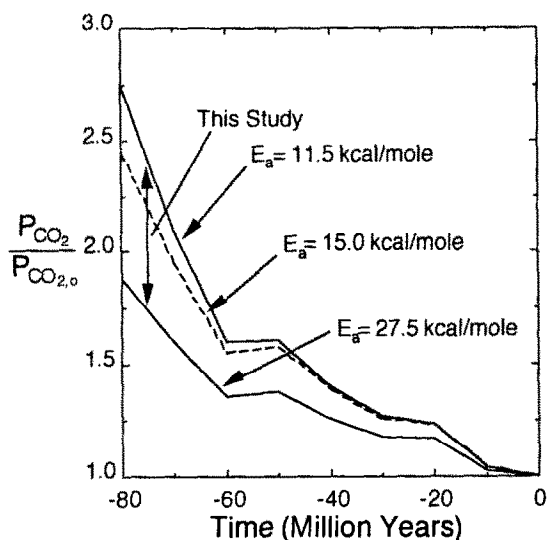


FIG. 3. P_{CO_2} values calculated with the model of BERNER (1991) using the feedbacks of this study and the updated weathering function of BERNER (1993) relative to their present-day values. The thick lines indicate relative paleo- P_{CO_2} values calculated from the results of this study.

the model of BERNER (1991) using both his updated feedback and ours. Note the obvious effect that changes in the dissolution activation energy have on the calculated P_{CO_2} . Paleo- P_{CO_2} values calculated with the activation energy for augite weathering are generally 30 to 40% less than those calculated with the activation energy for anorthite.

To predict the variation of atmospheric CO₂ over the lifespan of the Earth it is important to first accurately define carbon sources and sinks. LOVELOCK and WHITFIELD (1982) showed that with the advent of life the biota assumed control over the weathering feedback, moderating climate to their benefit. CALDEIRA and KASTING (1992) estimated the amount of CO₂ consumed by weathering in the face of increasing solar luminosity over the next 1.6 billion years. Their results indicate the minimum lifespan of the biosphere to be ~0.9 billion years. At that time atmospheric CO₂ levels will decrease below that required for photosynthesis by C4 plants. CALDEIRA and KASTING (1992) assumed no changes in geologic fluxes of CO₂ and used as their weathering input the temperature dependency originally used by WALKER et al. (1981) which ultimately came from the 100–200°C feldspar experiments of LAGACHE (1965) (and was subsequently used by MARSHALL et al., 1988). Substituting Eqn. 4 in the model of CALDEIRA and KASTING (1992) indicates that C4 plants may last as little as ~700 million years, or up to 200 million years less than CALDEIRA and KASTING (1992) calculate with their feedback (see Fig. 4). Silicate weathering in the face of an ever brighter Sun works to deplete CO₂ at a rapid rate, in the end shortening the lifetime of the weathering-climate feedback mechanism.

It should be re-emphasized that, like previous workers, we have used rate dependencies measured in the laboratory to simplistically model the effect of soil weathering reactions on atmospheric CO₂. The lab results are a useful starting model which can be expanded to point out and address more

complex weathering-climate interrelationships. Soil weathering depends on the amount of wetted surface area (e.g., SWOBODA-COLBERG and DREVER, 1992). Passivating organic films may inhibit dissolution. Changing vegetative cover may also affect overall rates of weathering. Each of these processes may in fact depend in a complicated fashion on temperature and, or CO₂. From the results of this study the specific effects of organic activity on the activation energies of dissolution are unclear. The activation energy measured for anorthite in acetic acid is similar to values calculated from previous studies (KNAUSS and WOLERY, 1986; CARROLL and WALTHER, 1990; HELGESON et al., 1984), some of which used organic buffers to control pH. It is less than that measured for albite dissolution in oxalic acid (16 kcal/mol; BRANTLEY, 1992). The activation energy for augite dissolution in acetic acid is high relative to other silicates, though not inconsistent with those measured for other chain silicates in organic-free solutions. The latter range from 11.7 kcal/mol for enstatite (SCHOTT et al., 1981) to 11.9–35.8 kcal/mol for diopside (SCHOTT et al., 1981). Overall our results are conservative as VELBEL (1993) has shown that activation energies in the field for feldspars are larger than those measured in the laboratory.

Increased P_{CO_2} has the potential to lower soil pH. Organic ligands protonate at lower pH, in the process losing their rate-accelerating effect. At the same time dissolution rates of silicates in organic-free solutions at pH < 5 increase with decreasing pH due to the action of protons adsorbed at the mineral surfaces. The net effect of decreasing pH on soil weathering will therefore reflect the displacement of rate-accelerating organic ligands by rate-promoting protons. Note also that silicate weathering in organic-free solutions between pH 5 and 8 is independent of pH. Decreases in soil pH brought about by increased P_{CO_2} would consequently have minimal indirect effect on organic-free weathering in near neutral solutions.

Activation energies for silicate dissolution generally increase somewhat with decreasing pH below pH 5 (CARROLL and WALTHER, 1990; BRADY and WALTHER, 1992; CASEY and SPOSITO, 1992). The effect of changing pH on activation energies for organic-mediated dissolution are unknown. Note

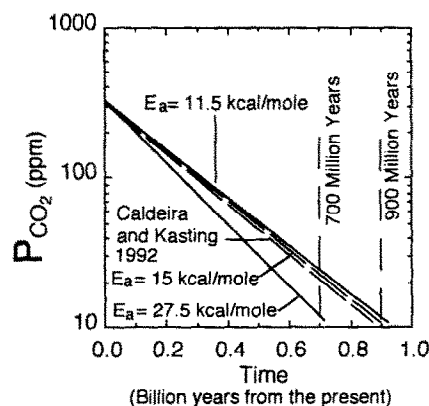


FIG. 4. Lifespan of the biosphere using the model of CALDEIRA and KASTING (1992), their feedback, and the weathering feedback of this study.

also that the degree to which P_{CO_2} , organic acid production, and soil pH are connected has yet to be determined. Soil pH is likely to be somewhat insensitive to changes in P_{CO_2} . Organic acids often rival carbonic acid in abundance in soils and would tend to buffer pH shifts in soil waters. Ion exchange and the accelerated weathering of the silicates themselves would also tend to anchor the pH of soils. Fertilization of organic acid production is therefore probably a far more important effect of increases in P_{CO_2} .

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